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EIGHTH QUARTERLY REPORT

Ending

April 27, 1963

PEM FOR PRODUCTION OF FLUORINATED BARIUM
TITANATE CAPACITORS FOR OPERATION TO 200°C

CONTRACT NO. DA-36-039-SC-85955
U. S. ARMY SIGNAL SUPPLY AGENCY
PHILADELPHIA, PENNSYLVANIA

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**CORNELL-DUBILIER
ELECTRIC CORPORATION**

CERAMIC DIVISION • NEW BEDFORD, MASSACHUSETTS

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By

CORNELL-DUBILIER ELECTRIC CORP.

Ceramic Division

New Bedford, Mass.

Approved by:


L. E. Nordquist
Chief Engineer
CERAMIC DIVISION

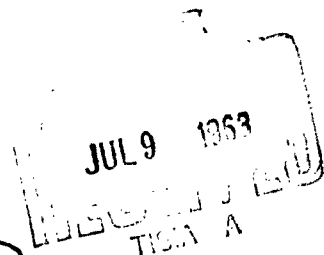


TABLE OF CONTENTS

	Page
1. ABSTRACT	1-1
2. PURPOSE	2-1
3. NARRATIVE AND DATA	3-1
3.1 Review	3-1
3.2 Bulk Fluorination	3-2
3.3 Glass Encapsulation	3-4
3.4 Encapsulants	3-5
3.5 Pre-Production Samples	3-6
4. CONCLUSION	4-1
5. PROGRAM FOR NEXT QUARTER	5-1

1. ABSTRACT

1.1 There appears to be a relationship between first firing conditions and fluoride tolerance. It is anticipated that experiments in short firing cycles will result in a more simplified fluorination technique.

1.2 Chemical analysis of Fluorine content in fluorinated dielectrics has been performed by TAM and is contained in this report. Variations in F content are possibly related to first firing techniques.

1.3 Dipped encapsulants capable of withstanding 200 C and providing good terminal support are being tested. The use of pre-molded cases is considered and will be evaluated.

1.4 Pre-production samples have been fluorinated and no difficulty is anticipated during qualification testing.

2. PURPOSE

2.1 The purpose of this project is to establish the capability to fluorinate 16,000 capacitor discs per eight hour shift and to manufacture 4,000 capacitors each of four types in accordance with Signal Corps Technical Requirements SCS-37 dated 9 March, 1959 and amendment No. 1 dated 29 November, 1960, and amendment No. 2 dated 8 January, 1963. This requirement defines the quality and testing program for 200°C fluorinated ceramic capacitors as listed below.

2.1.1 CK63 barium titanate capacitors rated at 10,000 mmf., $\pm 20\%$, 500 VDC at 85°C and 250 VDC at 200°C using barium titanate made with West German barium carbonate.

2.1.2 CK63 barium titanate capacitors rated at 10,000 mmf., $\pm 20\%$, 500 VDC at 85°C and 250 VDC at 200°C using barium titanate made with domestic barium carbonate.

2.1.3 Barium titanate capacitors, maximum diameter 0.39 inches rated at 10,000 mmf., $\pm 20\%$, 50 VDC at 85°C and 25 VDC at 200°C using barium titanate made with West German barium carbonate.

2.1.4 Barium titanate capacitors, maximum diameter 0.39 inches rated at 10,000 mmf., $\pm 20\%$, 50 VDC at 85°C and 25 VDC at 200°C using barium titanate made with domestic barium carbonate.

2.1.5 Amendment to SCS-37 requires that capacitors exceed a minimum terminal strength requirement of 5 pounds.

3. NARRATIVE AND DATA

3.1 REVIEW

3.1.1 Ceramic capacitors, MIL style CK63, capable of operating at 200°C, were manufactured from a fluorinated dielectric of which BaTiO_3 was the predominant material, 87%, other materials being CaZrO_3 , 12.7%; Fe_2O_3 , 0.1%; and Ce_2O_3 , 0.2%. A low voltage, miniaturized, fluorinated capacitor, having a thin dielectric of the same composition as the CK63 capacitors, has also been manufactured for 200°C operation. Fluorination of a dielectric can be accomplished by several means, but the method employed during this contract has been to re-fire the matured dielectric in a fluoride atmosphere. A special tunnel kiln of small cross sectional area, width - 4 1/2", height - 1 1/2", and hot zone length - 20", was constructed for this purpose. Capacitor discs are loaded on setters coated with ZrO_2 grain and pushed through the kiln at a controlled speed of approximately .33 inches per minute in the hot zone. The fluoride atmosphere is provided and maintained by regular additions of a donor tablet of volatile fluorides such as ZrF_4 . The time-temperature relationship, as well as the donor charge for this method of fluorination, is critical in that these variables must be determined by trial runs prior to each fluorination run. The kiln must be well conditioned, with volatile fluorides over an extended period of time to establish an equilibrium between the fluoride atmosphere and kiln refractories. The pilot run kiln presently being used is operated at 2400°F, with a soak period of one hour and a nominal donor charge of one gram per setter.

The dimensions of these setters are approximately 3 1/2" width, 5" length, and 3/4 height, and they are made from a slip cast zirconium silicate refractory mix.

3.1.2 Fluorinated capacitors have been manufactured, using glass encapsulation. These capacitors have met and exceeded all requirements as outlined in SCS-37 and have qualified for Pilot Run manufacturing. Problems of capacitance loss during glass encapsulation have been solved by using a higher silver content paint, DuPont silver No. 7713.

3.1.3 Low terminal strength properties of this capacitor are unsatisfactory and a modification has been implemented to require that capacitors meet a lead pull test of 5 pounds minimum per MIL-C-11015C. It is intended that an outer encapsulant of a more rugged material such as epoxy replace the present silicone rubber.

3.2 BULK FLUORINATION

3.2.1 Present capability of fluorination exceeds minimum requirements of 16,000 capacitor discs per eight hours. The variables associated with this operation require that fluorination conditions for each lot be carefully established by trial runs. Several hundred thousand discs have been fluorinated in an attempt to more fully understand and thereby control the parameters of this technique. Color changes in the discs are used as a visual control in monitoring fluoride additions during the runs. The significant feature to come out of all these firings is that some lots of capacitor discs have a wide tolerance level for fluorides and are very easily fluorinated

in large quantities with almost no monitoring required. Since compositions and raw material lots are the same, this condition of being readily fluorinated must originate during the first firing.

3.2.2 In order to more closely examine the effect of first or oxidized firing conditions on fluorination, a small temporary tunnel kiln is being constructed. This kiln will permit rapid firing and cooling, plus soaking times anywhere from five minutes to five hours. The tendency of titanate dielectrics to become semiconductors when overfired, is similar to that encountered when dielectrics are over-fluorinated. It has been established that an overfired disc is difficult to fluorinate and usually over-fluorinates as compared with more optimumly fired discs. Experiments with the new kiln will be centered around short firing times and relating this condition to fluoride tolerance. It is believed that discs can be thus prepared that will show a broad tolerance to fluorination conditions and make possible bulk fluorination of much larger quantities without constant operator supervision.

3.2.3 The variations of fluoride tolerance between discs has been confirmed by chemical analysis. Capacitor discs from the first two pre-production items which have been subjected to and passed various environmental tests have been examined for fluoride content. The splendid cooperation of the Signal Corps and Titanium Alloy Manufacturing Division of National Lead company, who offered their services and performed the analysis, is appreciated and acknowledged. The Fluorine content is reported in grams per gram of TiO_2 .

In this manner, the total content is a function of the percentage and can be used for comparison purposes.

The report is as follows:

	<u>Lot No. BaTiO₃</u>	<u>BaCO₃ Source</u>	<u>Environmental Test Performed</u>	<u>Fluorine Content gms gm TiO₂</u>
1	21-P	Imported	None(Silvered Discs)	.00369
2	26-C	Domestic	Vibration, temperature & immersion cycling	.00183
3	26-C	Domestic	2000 hr. life test, 200 C	.00385
4	21-P	Imported	Vibration, temperature & immersion cycling	.00285
5	21-P	Imported	2000 hr. life test, 200 C	.00269

3.2.4 The discrepancy of F content between Sample 2 and Sample 3 persists and it does not seem possible that the difference can be attributed to the environmental tests performed. All of the discs examined, exhibited an optimum fluorinated condition, as confirmed by electrical performance during qualification testing. This difference in F content closely resembles what has been previously referred to as fluoride tolerance and adds impetus to the need for further work on this phenomena as related to crystal development during first firing operations.

3.3 GLASS ENCAPSULATION

The reasons for the superior performance of the glass encapsulated fluorinated dielectric has not been fully understood. It has been clearly demonstrated that the addition of glass encapsulation has resulted in improved life test

characteristics. A possible explanation of the reason for this phenomena is related to proton migration from the anode. It is believed that hydrogen ion migration takes place from the positive electrode during voltage-life tests. A likely source for the hydrogen ion would be the adsorbed layer of water on the surface of most ceramic surfaces. The glass encapsulation, performed at high temperatures, shields the electrode from this film and prevents electrolysis of this type. This theory is offered as a possible explanation; however, confirmation is beyond the scope of this contract.

3.4 ENCAPSULANTS

3.4.1 The application of a rugged encapsulant over the glass coated capacitor has proven difficult. Epoxy base and Novalac resins are readily applied by dipping and do provide the necessary terminal support. Unfortunately, these resins, due to their strong adherence, fracture the discs during temperature cycling tests. A cooperative program with major suppliers of these resins is established. Special resin modifications presently on test appear excellent. Dipped capacitors are currently undergoing life tests at 200 C.

3.4.2 Ideal materials for 200 C operation are the silicones. Unfortunately, these materials do not lend themselves to dipping for thick coatings. A reasonable approach of using pre-molded cases with silicone potting materials has been discussed with suppliers. Materials are available for this technique which should conform to physical requirements. A second method, using silicones, would be transfer molding. This approach is being investigated but would require a molding press for production items.

3.4.3 Epoxy impregnated cements at first appeared quite successful but continued exposure to 200 C resulted in a cracking of this encapsulant. Further investigation of this approach has been discontinued in favor of either the modified dip or the use of pre-molded cases.

3.5 PRE-PRODUCTION SAMPLES

3.5.1 Dielectrics for all pre-production samples have been fluorinated pending development of a suitable encapsulant capable of meeting terminal strength requirement of MIL-C-11015C. These dielectrics appear to be satisfactory and no difficulty is expected in meeting test requirements of SCS-37.

3.5.2 A high speed temperature test chamber with a range of -100 F to +425 F has been purchased by Cornell-Dubilier to perform the complete temperature tests required. This chamber, Model SLHU-1-LC from Associated Testing Laboratories, Inc., should speed up measurements required during experimental and qualification testings. Approval of this chamber for test measurements will be requested.

4. CONCLUSION

4.1 Bulk fluorination techniques, though satisfactory, are being improved.

A relationship between first firing and fluorination tolerance is suspected and is being investigated.

4.2 The Fluorine content in the dielectrics ranges from approximately .00183 grams per gram of TiO_2 to .00385 grams. The wide variation appears to reflect the fluorination tolerance of individual discs.

4.3 The role of glass encapsulation as a barrier to proton migration has been postulated as a reason for the superior performance of this construction technique.

4.4 The high temperature resins presently available require modification for use as an encapsulant for ceramic capacitors. It might be necessary to use pre-molded cases and silicone potting materials for capacitor encapsulation.

4.5 Pre-production dielectrics have been fluorinated and await development of suitable encapsulants.

4.6 An improved, high speed, test chamber, has been purchased for use in obtaining high temperature measurements during qualification testing.

5. PROGRAM FOR NEXT QUARTER

5.1 Correlate first firing conditions with fluoride tolerance with the intention of simplifying fluorination procedure.

5.2 Establish encapsulating materials and procedures for use on all pre-production samples.

5.3 Submit 50V pre-production samples for qualification testing.